544278

PATENT COOPERATION TREATY

PCT

REC'D 10 MAR 2005
WIPO PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY
(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 62933A	**FOR FURTHER ACTION**	See Form PCT/IPEA/416
International application No. PCT/US2004/005018	International filing date *(day/month/year)* 20.02.2004	Priority date *(day/month/year)* 21.03.2003
International Patent Classification (IPC) or national classification and IPC C08F10/06, C08F2/00		
Applicant DOW GLOBAL TECHNOLOGIES, INC. et al.		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *sent to the applicant and to the International Bureau)* a total of 8 sheets, as follows:
      ☒ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:

☒	Box No. I	Basis of the opinion
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☐	Box No. VII	Certain defects in the international application
☐	Box No. VIII	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
16.09.2004	09.03.2005
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Thomas, D Telephone No. +49 89 2399-7837

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/US2004/005018

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

   ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3 and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4)
   - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages

1-6, 8, 9, 13-19, 21, 23-35	as originally filed
7, 10, 11, 12, 20, 22	filed with telefax on 17.08.2004

Claims, Numbers

1-6	filed with telefax on 17.08.2004

Claims, Pages

36-37	as originally filed

☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

* *If item 4 applies, some or all of these sheets may be marked "superseded."*

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-6
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-6
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-6
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1: US 3 919 185
D2: US 3 995 097
D3: US 5 034 481

1. None of the cited prior art documents disclose a catalyst composition combining a hydroxycarboxylate metal salt additive with a pi-bonded metallocene or with a group 4 metal complex as described in claim 1 of the present application.

2. Inventive step:

2.1 Document D1, which is considered to represent the most relevant state of the art, discloses a catalyst composition for the polymerization of alkenes.

2.2 The subject matter of claim 1 of the present application differs from D1 in that D1 dose neither disclose metallocenes or group 4 metal complexes as disclosed in claim 1 of the present application for the polymerization of olefines.

2.3 The objective technical problem to be solved is to improve process operability for metallocene type catalysts.

2.4 None of the cited prior art documents disclose or suggest to use hydroxycarboxylate metal salts as additives for metallocene type catalysts.

2.5 As a consequence the subject matter of claims 1-6 is inventive over D1 - D3.

3. M^b in line 10 of claim 3 should be replaced by M^q

Conventional-type chromium catalyst compounds, often referred to as Phillips-type catalysts, suitable for use in the present invention include CrO_3 , chromocene, silyl chromate, chromyl chloride (CrO_2Cl_2), chromium-2-ethyl-hexanoate, and chromium acetylacetonate ($Cr(AcAc)_3$). Non-limiting examples are disclosed in U.S. Patent Nos. 2,285,721, 3,242,099 and 3,231,550.

Still other conventional-type transition metal catalyst compounds suitable for use in the present invention are disclosed in U.S. Patent Nos. 4,124,532, 4,302,565, 4,302,566 and 5,763,723 and EP-A-416815 and EP-A-420436. The conventional-type transition metal catalysts of the invention may also have the general formula $M^c_tM^d X^a_{2t}Y^a_uE^a$, where M^c is Mg, Mn and/or Ca; t is a number from 0.5 to 2; M^d is a transition metal, preferably Ti, V and/or Zr; X^a is a halogen, preferably Cl, Br or I; Y^a may be the same or different and is halogen, alone or in combination with oxygen, $-NR^y_2$, $-OR^y$, $-SR^y$, $-COOR^y$, or $-OSOOR^y$, where R^y is a hydrocarbyl radical, in particular an alkyl, aryl, cycloalkyl or arylalkyl radical, acetylacetonate anion in an amount that satisfies the valence state of M^c; u is a number from 0.5 to 20; E^a is an electron donor compound selected from the following classes of compounds: (a) esters of organic carboxylic acids; (b) alcohols; (c) ethers; (d) amines; (e) esters of carbonic acid; (f) nitrites; (g) phosphoramides, (h) esters of phosphoric and phosphorus acid, and (j) phosphorus oxychloride. Non- limiting examples of complexes satisfying the above formula include: $MgTiCl_5 \cdot 2CH_3COOC_2H_5$, $Mg_3Ti_2Cl_{12} \cdot 7CH_3COOC_2H_5$, $MgTiCl_5 \cdot 6C_2H_5OH$, $MgTiCl_5 \cdot CH_3OH$, $MgTiCl_5 \cdot (THF)$, $MgTi_2C1_2 \cdot 7C_6H_5CN$, $Mg_3Ti_2Cl_{12} \cdot 6C_6H_5COOC_2H_5$, $MgTiCl_6 \cdot 2CH_3COOC_2H_5$, $MgTiCl_6 \cdot 6C_5H_5N$, $MgTiCl_5(OCH_3) \cdot 2CH_3COOC_2H_5$, $MgTiCl_5N(C_6H_5)_2 \cdot 3CH_3COOC_2H_5$, $MgTiBr_2Cl_4 \cdot 2(C_2H_5)_2O$, $MnTiCl_5 \cdot 4C_2H_5OH$, $Mg_3V_2Cl_{12} \cdot 7CH_3COOC_2H_5$, $MgZrCl_6 \cdot 4(THF)$. Other catalysts may include cationic catalysts such as $AlCl_3$, and other cobalt and iron catalysts well known in the art.

Typically, these conventional-type transition metal catalyst compounds excluding some conventional-type chromium catalyst compounds are activated with one or more of the conventional-type cocatalysts described below.

Conventional-Type Cocatalysts

Conventional-type cocatalyst compounds for the above conventional-type transition metal catalyst compounds may be represented by the formula $M^e M^f_v X^b_c R^z_{e+v-c}$, wherein M^e is a metal from Groups 1, 2, 12 or 13 of the Periodic Table of Elements having a valency of e; M^f is a metal of Group 1 of the Periodic Table of Elements; v is a number from 0 to 1; each X^b is any halogen; c is a number from 0 to 3; and each R^z is a monovalent hydrocarbon radical or

and disubstituted boron radicals including dimethylboron for example; and disubstituted pnictogen radicals including dimethylamine, dimethylphosphine, diphenylamine, methylphenylphosphine, chalcogen radicals including methoxy, ethoxy, propoxy, phenoxy, methylsulfide and ethylsulfide. Non-hydrogen substituents R include the atoms carbon, silicon, nitrogen, phosphorous, oxygen, tin, and germanium including olefins such as but not limited to olefinically unsaturated substituents including vinyl-terminated ligands, for example but-3-enyl, 2-vinyl, or hexene-1. Also, at least two R groups, preferably two adjacent R groups are joined to form a ring structure having from 4 to 30 atoms selected from carbon, nitrogen, oxygen, phosphorous, silicon, germanium, boron or a combination thereof. Also, an R group such as 1- butanyl may form a carbon sigma bond to the metal M.

Other ligands may be bonded to the transition metal, such as a leaving group Q. Q may be independently monoanionic labile ligands having a sigma- bond to M. Non-limiting examples of Q include weak bases such as amines, phosphines, ether, hydroxycarboxylates, dienes, hydrocarbyl radicals having from 1 to 20 carbon atoms, hydrides or halogens, and combinations thereof. Other examples of Q radicals include those substituents for R as described above and including cyclohexyl, heptyl, tolyl, trifluromethyl, tetramethylene and pentamethylene, methylidene, methyoxy, ethyoxy, propoxy, phenoxy, bis(N-methylanilide), dimethylamide, and dimethylphosphide radicals.

In addition, catalyst compounds of the invention are those where L^a and L^b are bridged to each other by a bridging group, E^b. These bridged compounds are known as bridged, catalyst compounds. Non- limiting examples of bridging group E^b include bridging radicals of at least one Group 14 atom, such as but not limited to carbon, oxygen, nitrogen, silicon, germanium and tin, preferably carbon, silicon and germanium, most preferably silicon. Other non-limiting examples of bridging groups, E^b, include dimethylsilyl, diethylsilyl, methylethylsilyl, trifluoromethylbutylsilyl, bis(trifluoromethyl)silyl, di-n-butylsilyl, silylcyclobutyl, di-i-propylsilyl, di-cyclohexylsilyl, di-phenylsilyl, cyclohexylphenylsilyl, t-butylcyclohexylsilyl, di-t-butylphenylsilyl, di(p-tolyl)silyl, dimethylgermyl, diethylgermyl, methylene, dimethylmethylene, diphenylmethylene, ethylene, 1-2-dimethylethylene, 1,2- diphenylethylene, 1,1,2,2-tetramethylethylene, dimethylmethylenedimethylsilyl, methylenediphenylgermyl, methylamine, henylamine, cyclohexylamine, methylphosphine, phenylphosphine, and cyclohexylphosphine.

Other catalysts compounds useful in the invention include metal complexes corresponding to the formula: $L_jM^bX_pX'_q$ (II)

wherein: M^b is a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of +2, +3 or +4, bound in an η^5 bonding mode to one or more L groups;

L independently each occurrence is a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, tetrahydrofluorenyl-, or octahydrofluorenyl- group optionally substituted with from 1 to 8 substituents independently selected from the group consisting of hydrocarbyl, halo, halohydrocarbyl, aminohydrocarbyl, hydrocarbyloxy, dihydrocarbylamino, dihydrocarbylphosphino, silyl, aminosilyl, hydrocarbyloxysilyl, and halosilyl groups containing up to 20 non-hydrogen atoms, or further optionally two such L groups may be joined together by a divalent substituent selected from hydrocarbadiyl, halohydrocarbadiyl, hydrocarbyleneoxy, hydrocarbyleneamino, siladiyl, halosiladiyl, and divalent aminosilane, groups containing up to 20 non-hydrogen atoms;

X independently each occurrence is a monovalent or polyvalent anionic ligand group having one or more shared of donative bonds to M^b, and optionally one or more shared or donative bonds to one or more L groups, said X containing up to 60 nonhydrogen atoms;

X' independently each occurrence is a neutral Lewis base ligating compound, having up to 20 atoms;

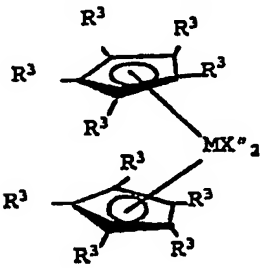
j, p, and q are 0, 1 or 2.

The compositions of the present invention are believed to exist in the form of a mixture of one or more cationic, zwitterionic or other catalytically active species derived from the foregoing metal complex a) in combination with the activator compound, b), or alternatively, a mixture of the metal complex or a cationic, zwitterionic or other catalytically active derivative thereof with a derivative formed by interaction of compound c) with the cocatalyst or with the activated catalyst. Fully cationic or partially charge separated metal complexes, that is, zwitterionic metal complexes, have been previously disclosed in US-A-5,470,993 and 5,486,632. Derivatives of the Group 13 compound and cocatalyst may arise, for example, by ligand exchange. In particular, where the cocatalyst is a strong Lewis acid, such as tris(fluorophenyl)borane, some quantity of fluorophenyl substituents may exchange with the ligand groups of the Group 13 compound to form fluorophenyl substituted derivatives thereof.

Preferred X' groups are phosphines, especially trimethylphosphine, triethylphosphine, triphenylphosphine and bis(1,2-dimethylphosphino)ethane; $P(OR)_3$, wherein R is as previously defined; ethers, especially tetrahydrofuran; amines, especially pyridine, bipyridine, tetramethylethylenediamine (TMEDA), and triethylamine; olefins; and conjugated dienes

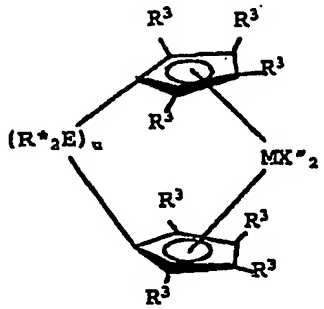
having from 4 to 40 carbon atoms. Complexes including conjugated diene X' groups include those wherein the metal is in the +2 formal oxidation state.

Preferred examples of coordination complexes used according to the present invention include the following species:



(III)

or



(IV)

wherein:

M is as previously defined, more preferably titanium, zirconium or hafnium, most preferably zirconium or hafnium, in the +2 or +4 formal oxidation state;

R^3 in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, said R^3 having up to 20 non-hydrogen atoms, or adjacent R^3 groups together form a divalent derivative (that is, a hydrocarbadiyl, siladiyl or germadiyl group) thereby forming a fused ring system,

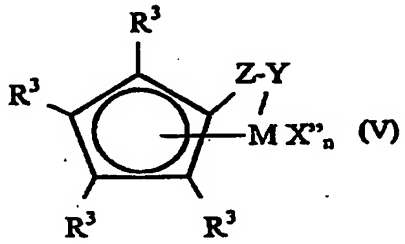
X" independently each occurrence is an anionic ligand group of up to 40 non-hydrogen atoms, or two X" groups together form a divalent anionic ligand group of up to 40 non-hydrogen atoms or together are a conjugated diene having from 4 to 30 non-hydrogen atoms forming a π-complex with M, whereupon M is in the +2 formal oxidation state,

R* independently each occurrence is C_{1-4} alkyl or phenyl,

E independently each occurrence is carbon or silicon, and

u is an integer from 1 to 8.

Additional examples of suitable metal complexes correspond to the formula:



(V)

wherein:

diyl)methane)]hafnium di(N,N-dimethylamido),

[N-(2,6-di(1-methylethyl)phenyl)amido)(o-tolyl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride,

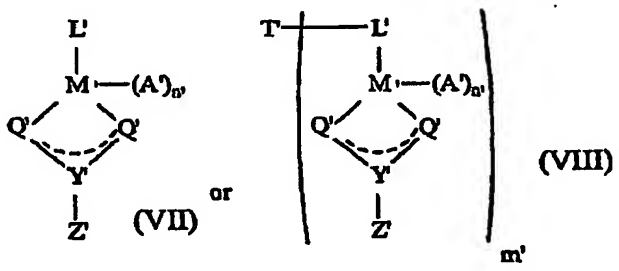
[N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl,

[N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(N,N-dimethylamido), and

[N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride.

The foregoing types of catalysts and catalyst compositions are described in, for example, U.S. Patent's 5,703,187, 5,965,756, 6,150,297, 5, 064,802, 5,145,819, 5,149,819, 5,243,001, 5,239,022, 5,276,208, 5,296,434, 5,321,106, 5,329,031, 5,304,614, 5,677,401 and 5,723,398, PCT publications WO 93/08221, WO 93/08199, WO 95/07140, WO 98/11144, WO02/02577, WO 02/38628; and European publications EP-A-578838, EP-A-638595, EP-A-513380 and EP-A-816372.

Additional suitable catalyst compound are complexes of a transition metal, a substituted or unsubstituted π-bonded ligand, and one or more heteroallyl moieties, such as those described in U.S. Patents 5,527,752 and 5,747,406, and EP- B-0 735 057. Preferably, these catalyst compounds are represented by one of the following formulas:



wherein M' is a metal from Groups 4, 5 or 6 or the Periodic Table of the Elements, preferably titanium, zirconium or hafnium, most preferably zirconium or hafnium;

L' is a substituted or unsubstituted, π-bonded ligand coordinated to M' and, when T' is present, bonded to T', preferably L' is a cycloalkadienyl ligand, optionally with one or more hydrocarbyl substituent groups having from 1 to 20 carbon atoms, or fused ring derivatives thereof, for example, a cyclopentadienyl, indenyl or fluorenyl ligand;

each Q' is independently selected from the group consisting of -O-, -NR'-, -CR'$_2$- and -S-, preferably oxygen;

Y' is either C or S, preferably carbon;

AMENDED SHEET

Based Catalysts for Polymerization of Ethylene and a-Olefins", J.A.C.S. (1995) 117, 6414-6415 and Johnson, et al., "Copolymerization of Ethylene and Propylene with Functionalized Vinyl Monomers by Palladium(II) Catalysts", J.A.C.S., (1996) 118, 267-268, and WO 96/23010, may be combined with a hydroxycarboxylate metal salt for use in the process of invention. These complexes can be either dialkyl ether adducts, or alkylated reaction products of the described dihalide complexes that can be activated to a cationic state by the conventional-type cocatalysts or the activators of this invention described below.

Also included as catalyst compounds are those diimine ligand based Group 8 to 10 metal compounds disclosed in PCT publications WO 96/23010 and WO 97/48735 and Gibson, et al., Chem. Comm., 849-850 (1998).

Other catalysts are those Group 5 and 6 metal imido complexes described in EP-A-0 816 384 and U.S. Patent 5,851,945. In addition, catalysts include bridged bis(arylamido) Group 4 compounds described by D. H. McConville, et al., Organometallics (1995) 14, 5478-5480. Other catalysts are described as bis(hydroxy aromatic nitrogen ligands) in U.S. Patent 5,852,146. Other metallocene-type catalysts containing one or more Group 15 atoms include those described in WO 98/46651. Still another metallocene-type catalysts include those multinuclear catalysts as described in WO 99/20665.

It is contemplated in some embodiments, that the catalyst compounds of the invention described above may be asymmetrically substituted in terms of additional substituents or types of substituents, and/or unbalanced in terms of the number of additional substituents on the π-bonded ligand groups. It is also contemplated that the catalysts of the invention may include their structural or optical or enantiomeric isomers (meso and racemic isomers) and mixtures thereof, or they may be chiral and/or a bridged catalyst compounds.

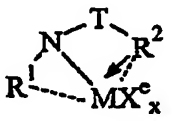
Activator and Activation Methods For the Catalyst Compounds

The above described catalyst compounds for use in the invention are typically activated in various ways to yield catalyst compounds having a vacant coordination site that will coordinate, insert, and polymerize olefin(s).

For the purposes of this patent specification and appended claims, the term "activator" is defined to be any compound or component or method which can activate any of the catalyst compounds of the invention as described above. Non-limiting activators, for example may include a Lewis acid or a non-coordinating ionic activator or ionizing activator or any other compounds including Lewis bases, aluminum alkyls, conventional-type cocatalysts (previously described herein) and combinations thereof that can convert a neutral catalyst compound to a catalytically active cation. It is within the scope of this invention to use

CLAIMS:

1. A catalyst composition comprising a catalyst compound selected from π-bonded metallocenes and Group 4 metal complexes of the formula ,



wherein

R^1 is selected from alkyl, cycloalkyl, heteroalkyl, cycloheteroalkyl, aryl, and inertly substituted derivatives thereof containing from 1 to 30 atoms not counting hydrogen;

T is a divalent bridging group of from 1 to 20 atoms other than hydrogen,

R^2 is a C_{6-20} heteroaryl group containing Lewis base functionality, a pyridin-2-yl-, or a substituted pyridin-2-yl group,

M is the Group 4 metal,

X^c is an anionic, neutral or dianionic ligand group,

x is a number from 0 to 5 indicating the number of such X^c groups, and

bonds, optional bonds and electron donative interactions are represented by lines, dotted lines and arrows respectively;

an activator capable of converting said catalyst compound into an active catalyst for addition polymerization, optionally a carrier, further optionally a liquid diluent, and a hydroxycarboxylate metal salt additive.

2. A catalyst composition according to claim 1 wherein the hydroxycarboxylate metal salt is a hydroxy-substituted, mono-, di- or tri-carboxylic acid salt wherein the metal portion is a cationic derivative of a metal from Groups 1-13 of the Periodic Table of Elements.

3. A catalyst composition according to claim 1 wherein the metal salt is represented by the following general formula:

$M^q(Q^a)_{q'}(OOCQ^b)_{q''}$, where

M^q is a metal from Groups 1 to 16 and the Lanthanide and Actinide series;

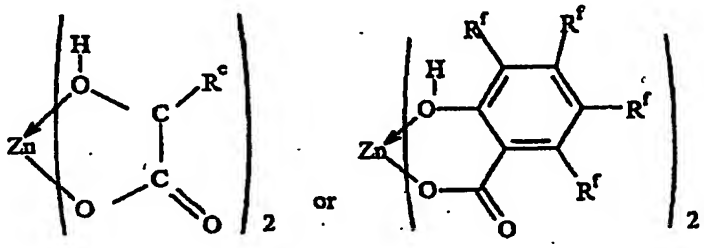
Q^a is halogen, hydrogen, hydroxide, or an alkyl, alkoxy, aryloxy, siloxy, silane, sulfonate or siloxane group of up to 20 atoms not counting hydrogen;

Q^b is a hydrocarbyl radical having from 1 to 50 carbon atoms, and optionally substituted with one or more hydroxy, alkoxy, N,N-dihydrocarbylamino, or halo groups, with the proviso that in one occurrence Q^b is substituted with a hydroxy- group that is coordinated to the metal, M^b by means of unshared electrons thereof;

q' is an integer from 0 to 3;

q" is an integer from 1 to 4.

4. A catalyst composition according to claim 1 wherein the hydroxycarboxylate metal salt corresponds to the formula:



wherein R^c and R^f independently each occurrence are hydrogen, halogen, or C_{1-6} alkyl.

5. A catalyst composition according to claim 1 wherein the catalyst compound is a metallocene.

6. An olefin polymerization process wherein one or more olefin monomers are polymerized in the presence of a catalyst composition characterized in that the catalyst composition corresponds to any one of claims 1-5.